(12) UK Patent Application (19) GB (11) 2 105 735 A

(21) Application No 8225215
(22) Date of filing 3 Sep 1982
(30) Priority data
(31) 56/142430
(32) 11 Sep 1981
(33) Japan (JP)
(43) Application published
30 Mar 1983
(51) INT CL^3
C08L 75/04 C09D
11/10 // C08J 3/20
(52) Domestic classification
C3R 32D1 32D6C 32D6K
32D8 32E10 32E1 32E2A
32E2DX 32E2E 32E2Y
32E3A 32E3D 32E3Y 32E4
32G2A 32G2Y 32H1
32H5B2 32H5BY 32H8
32H9A 32J1A 32J1Y
32J2C 32J2D 32J2E
32J2F 32J2X 32J2Y
32J3A 32J3B 32J3Y
32J7A 32J7Y 32KH 32S
32T2B C11 C12 C13M
C13S C14B C16 C21 C25
C26 C29 C33A C33X C6X
C8R C9N C9Q L2A L2X L3A
L3B L5D L5X L6G LA LC V
U1S 1390 2236 3032 C3R
(56) Documents cited
EP A1 0014921
GBA 2046770
GB 1558690
GB 1575637
GBA 2078762
(58) Field of search
C3R
C3V
C3M
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(54) **Ink composition for ink jet printing**

(57) An ink composition for ink jet printing comprises an aqueous medium in which are dispersed particles of a polyurethane latex containing a dye.

GB 2 105 735 A

SPECIFICATION
Ink composition for ink-jet printing

The present invention relates to an ink composition for ink-jet printing, and more particularly to the ink composition for ink-jet printing comprising a polymer latex particle containing a dye.

Ink-jet recording method is to print information by jetting, with controlling an ink liquid, an ink droplet thereof onto a recording medium without bringing a printing head into contact with said recording medium, and have been adopted for terminal printer systems and the like and have come into wide use in recent years because of the advantage that the method has no noise during the printing and enables a high-speed printing on an ordinary paper.

Conventionally known ink-jet printing processes include those of a pressurized oscillation type (including a charging quantity control process, an electric field control process, a binary control process, a scattering angle control process and the like); of an electrostatic acceleration type; and of a pressure pulse type of an impulse jet type, and the like; that is, there are known the ink-jet process wherein an ink droplet jet is caused by the abrupt reduction of the volume of an ink chamber or by pressing out or sucking in by a given pressure; the ink-jet process wherein an ink is jetted accelerately and electrostatically from a nozzle by the signal voltage applied to between the nozzle and an electrode opposite thereto, and the ink-mist process wherein ink-mist is brought about by ultrasonic oscillation.

Characteristics required for the ink composition for the above-mentioned ink-jet printing processes and ink-mist process are that:

i) the ink is to have a sufficient concentration for printing,
ii) it is not to be evaporated and dried (i.e., not to clog) inside the nozzle of a printing head,
iii) it is to be dried upon the ink by the attachment of an ink droplets onto the surface of paper,
iv) the once printed ink is not to be blurred by water or sweat, or a printed portion is not to be vanished, and
v) no changes in the physical properties of the ink nor deposits in the ink are to occur during the storage.

There have heretofore been known an ink composition for ink-jet printing as, for example, those prepared by dissolving water-soluble acid dye or basic dye into water and top the solution are added such additives as wetting agent, antiseptic, and the like. However, above ink composition, because dye is soluble in water, have the disadvantages that the printed ink is blurred by water or sweat, or the printed portion becomes vanished, and in addition, in the case of color printing, the color printed becomes turbid, because of the mixing of inks in different colors.

In contrast, those ink compositions have been known which comprise polymer latex into which dyes are incorporated. For example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) No. 146109/1979 discloses such ink composition as comprising a vinyl polymer particle containing hydrophobic dye and an aqueous medium prepared by dissolving water-soluble dye in water, while Japanese Patent O.P.I. Publication No. 139471/1980 discloses ink composition that dispersed dye is present in the condition of being impregnated in a water-insoluble vinyl polymer latex particle.

These ink compositions comprising polymer latex are advantageous in that because the dye therein is protected by the polymer latex thereof unlike those comprising water-soluble dyes only, said ink compositions may not be blurred by water or sweat, and because it may be made glossy, quality of printed letters by the ink may be improved thereof.

However, the vinyl polymer latex is disadvantageous in that the impregnating amount of the dye is small and the storability of the impregnated dye is not sufficient. Furthermore, as in the above two examples, in the case where the dye is rendered present in the medium in order to increase the density of printed dots, it is certain that a sufficient dot density can be obtained, but on the contrary, there occurs blur, resulting in the deformation of true round of the dot.

It is an object of the present invention to provide an ink composition for an ink-jet printing, which said composition is free of the above-mentioned disadvantage as observed in those conventional ink compositions containing a latex and which gives high concentration and truly round printed dots having a high density of printed letters, and further has satisfactory stability during the storage thereof.

The above-mentioned object of the present invention may be attained by an ink-jet recording ink composition comprising dye-containing polymer latex particles and an aqueous medium necessary to disperse the particles, which polymer latex particles comprise a polyurethane polymer.

Preferable ink-jet printing method capable of attaining the above-mentioned object of the present invention is an ink-jet printing method that the ink-jet recording ink composition comprising dye-containing polymer latex particles and an aqueous medium necessary to disperse the particles, which polymer latex particles comprise a polyurethane polymer, is used to be filled in a pressure chamber that is opened to a nozzle, which pressure chamber is so constructed that at least a portion of the chamber wall can be deformed by electromechanically converting means, and the pressure chamber wall, when applying an electrically driving pulse thereto, is inwardly displaced by the action of the electromechanically converting means to thereby abruptly reduce the inside volume of the pressure chamber, causing a part, as a drop, of the amount of the ink composition filled in the pressure chamber to jet from the nozzle toward the recording medium, thus jetting one drop of the ink per driving pulse,

and after that, the volume of the pressure chamber is restored to the original state to regain the original equilibrium ink condition.

According to the present invention, a high density-having and stably jet-recordable ink-jet recording ink composition can be obtained.

Generally, polyurethane latexes have a higher degree of being impregnated with hydrophobic dye than have vinyl polymer latexes; that is, polyurethane latex is capable of being stably impregnated with much quantity of hydrophobic dye per weight of the latex over a long period of time. Further, in the ink composition dispersed the latex, if said latex particle concentration was increased, the dispersion stability of said ink composition thereof become extremely deteriorated. Therefore, because of impregnation degree of the vinyl polymer latex is small, it is difficult to prepare any stable ink composition capable of a high concentration for printing.

In addition, the polyurethane latex, as compared to the vinyl polymer latex, is capable of being impregnated with various kinds of hydrophobic dyes in a wide range, and therefore, suitable for use in the ink composition for color ink-jet printing.

In the case of the vinyl polymer latex, if the kind of a dye to be used is changed, there are cases where the composition of the polymer must be changed, whereas in the case of the polyurethane latex, the substantially same composition may well be used, and therefore, it has wider acceptability to dyes.

Further, the polyurethane latex is excellent in the preserved stability of impregnated hydrophobic dye during the storage. The diameter of an orifice for the ink-jet nozzle applicable to ink-jet printing is as small as from 50 to 100 μm, so that the most care must be taken to prevent deposits of the ink composition or foreign matters, but the hydrophobic dye, although it becomes depositing with time in a short period in the case of the vinyl polymer latex, is capable of being present sufficiently stably in the polyurethane latex during the storage over extensive periods. For such reasons, the polyurethane latex is a suitable polymer latex for an ink composition for ink-jet printing and enables to provide required properties therefore. A polyurethane latex is subsequently illustrated in detail below.

A preferred polyurethane may be derived from a polyol component and an isocyanate component, the polyol being comprised of:

(a) A kind of prepolymer or a prepolymer mixture which has at least two hydroxy terminal group and a molecular weight of from 300 to 20,000 and whose repeating unit is a lower alkyl ether or a lower alkyl ester, the prepolymer or the prepolymer mixture being in the quantity of from 10 to 100 mole% of that of the polyol to be present, and

(b) a low molecular weight diol with or without a functional group that donates positive charge or negative charge, the diol being in the quantity of from 90 to 10 mole% of that of the polyol to be present.

The preferred isocyanate component corresponds to the formula [I]:

$$O{=}C{=}N{-}R{-}N{=}C{=}O \qquad [I]$$

wherein R is represented by an alkylene group, a cycloalkylene group (preferable 5—7 membered ring), an arylene group, (preferable a phenylene group or a naphthylene group) an alkylene-bisarylene group or an arylene-bisalkylene group.

A particularly preferred polyurethane latex is derived from a prepolymer containing a caprolactone. Useful polyurethane latexes are described in U.S. Patent Nos. 2,968,575, 3,213,049, 3,294,724, 3,565,844, 3,388,087, 3,479,310, and 3,873,484. Generally, the polyurethane latex is produced by extending the chain of the prepolymer whose is the reaction product of a diisocyanate with an organic compound having two active hydrogen atoms. Those useful organic compounds having two active hydrogen atoms include polyalkylene ether glycols, alkyd resins, polyesters and polyesteramides. The polyurethane latex is generally produced in the manner that the prepolymer is emulsified, and the chain of said prepolymer is then extended in the presence of a chain-extending agent, e.g., water.

Useful polyurethane latex may be stabilized under the nonionic, anionic or cationic condition. Those polyurethane latexes stabilized under the anionic or cationic condition may be formed by combining a group having a charge with the polyurethane. The group useful for giving negative charge to the latex includes carboxylates, sulfonates, and the like. The useful repeating unit may be derived from a polyol having an active functional group, for example, 2,2-bis(hydroxymethyl)propionic acid, N,N-bis(2-hydroxyethyl)glycine. The useful group for giving positive charge to the latex include a quaternary amines, a sulfonium salts, phosphinates, and the like. The useful repeating unit may be derived from a polyol monomer having a tertiary amine group or a thio-functional group, for example, N-methyl-diethanolamine, 2,2-thioethanol, and the like. Those useful examples of the polyurethane latex stabilized by cation and the polyurethane latex stabilized by anion are described in U.S. Patent No. 3,479,310. Particularly useful examples are those stabilized by cation as described in U.S. Patent No. 3,873,484.

Preferred polyurethane latex is represented by the following formula [II]:

$$\left[\begin{array}{l} \left(R^1 \right)_x \\ \left(Z - R^2 - Z \right)_y \end{array} \underset{\substack{\| \\ O}}{C}NHR'NH\underset{\substack{\| \\ O}}{C} \right]_w \qquad (II)$$

wherein R′ represents an alkylene group having from 2 to 40 carbon atoms, an alkylene group containing hetero atom such as oxygen, a cycloalkylene group (preferable 5—7 membered ring) such as cyclohexylene, alkylene-biscyclohexylene and isophorone-1,4-diyl, an arylene group such as phenylene, naphthylene and tolylene, an alkylene-bisarylene group, or an arylene-bisalkylene group, these groups have preferably from 6 to 15 carbon atoms; R^1 represents

$$\text{—}(ZR^3)_m\text{—}(Z\text{—}(\underset{\substack{\| \\ O}}{C})_m R^4)_n\text{—}Z\text{— or}$$

$$\text{—}Z\text{—}(R^5\text{—}Z\text{—}\underset{\substack{\| \\ O}}{C}\text{—}R^6\text{—}\underset{\substack{\| \\ O}}{C}\text{—}Z)_p\text{—}R\text{—}Z\text{—};$$

R^2, R^3 and R^5 each represent an alkylene group having 2—10 carbon atoms, a cycloalkylene-bis (oxyalkylene) group such as 1,4-cyclohexylene-bis(oxyethylene), an arylene-bisalkylene group such as phenylene-bismethylene, and a poly(alkyleneoxyd) group consisting of from 2 to 500 repeating units whose alkylene portions each has from 2 to 5 carbon atoms; R^4 represents an alkylene group having from 2 to 10 carbon atoms; R^6 represents an alkylene group having from 2 to 10 carbon atoms or an arylene group; Z represents —O— or —NH—, p and n each represent an integer of from 2 to 500; m represents 0 or 1; y represents from 0 to 90 mole% of the diol component; x is from 100 to 10 mole% of the y; and w is from 1.1 to 2.0.

The minimum amount of the isocianate is the amount sufficient to produce terminal isocyanate groups on both ends of the prepolymer; i.e., a little more than 1 mole of the diisocyanate per mole of the diol; that is, z equals 1. This ratio would be more advantageous if it is 1 mole of the diol to nearly 2 mole of the diisocyanate.

Particularly advantageous polyurethane latex may be derived from a polycaprolactone whose both ends are protected with a glycol. Such polyurethane may be represented by the aforementioned formula wherein m is 1 and z is —O—.

As the polyol and the diisocyanate those various kinds may be used; useful polyols:

(1) Diols, e.g., alkylene diol having from 2 to 10 carbon atoms, arylene diol e.g., hydroquinone and those polyalkylene glycols represented by the formula: $HO(RO)_nH$ (wherein R is an alkylene group). e.g., poly(propylene)glycol, Pluracol P—2010 Pluracol P—1010 (available from BASF) and Niax PPG 2023 (available from Union Carbide),

(2) triols, e.g., glycerol, 2-ethyl-2-hydroxy-methyl-1,3-propanediol, 1,1,1-trimethylol-propane and 1,2,6-hexanetriol, and

(3) tetraols, e.g., pentaerythritol, higher polyols than this, such as, e.g., sorbitol and poly(oxyalkylene)derivatives of the foregoing polyols.

Other preferred polyols include a linear polyesters, and a block copolymers with ethyleneoxyde and propyleneoxyde and diamines e.g., ethylenediamine, which have hydroxy groups at the ends thereof, low acid value and low water content, and molecular weight of about 500, respectively and a caprolactone polymers having hydroxy groups at the ends thereof.

Those useful diisocyanates applicable to the present invention may be typified by 2,4- and 2,6-toluene diisocyanate, diphenyl methane-4,4′-diisocyanate, polymethylene-diphenylene isocyanate, bitoluene diisocyanate, dianisidine diisocyanate, 1,5-naphthalene diisocyanate, 1,6-hexamethylene diisocyanate, bis(isocyanate cyclohexyl)methane diisocyanate, isophorone diisocyanate, 2,2,4-trimethyl hexane diisocyanate and xylene diisocyanate.

The prepolymer is generally produced in the manner that the polyol and diisocyanate are mixed with stirring in a nitrogen gas flow, and a useful temperature for this reaction is from about 25 to 110°C. The reaction may be advantageously carried out in the presence of a solvent, if necessary, together with a catalyst. Useful solvent for the reaction include ketones and esters, aliphatic hydrocarbons such as a heptane, a octane, etc., and alicyclic hydrocarbons such as a methyl cyclohexane. Those useful catalysts include tertiary amines, acids and organic metallic compounds such as, e.g., triethylamine, stannous chloride, and di-n-butyl-tin dilaurate. If both polyol and isocyanate are liquid and the prepolymer also is liquid, the use of the organic solvent is not essential.

After producing a prepolymer, the prepolymer is emulsified and the chain thereof is extended in the presence of water to thereby prepare a latex. The emulsification of the prepolymer may be performed in the presence of a surfactant. Where the prepolymer contains an electric charge group, any further addition of the surfactant is unnecessary. The chain extention of the prepolymer may be effected by the addition of a chain-extending agent to the emulsified prepolymer.

Useful chain-extending agent is a compound containing at least two functional groups having an active hydrogen atom, typical examples of which include water, a hydrazine, primary and secondary amines, aminoalcohols, amino acids, oxyacids, diols, or mixtures of these compounds. Advantageous ones among the above chain-extending agents is a water, or a primary or secondary diamines. Advantageous diamines is 1,4-cyclohexene-bis(methylamine), ethylenediamine, or diethylenetriamine. The amount of the chain-extending agent is equal to the isocyanate equivalent of the prepolymer.

The particle size of the polyurethane latex preferably usable in the present invention is within the range of from 0.01 μ to 1.0 μ, and particularly preferably from 0.02 μ to 0.5 μ.

Dyes to be used in the present invention may be of any kind if capable of being impregnated in the polyurethane latex, but those hydrophobic are particularly preferred. Those applicable hydrophobic dyes include organic solvent-soluble monoazo dyes, anthraquinone dyes, metal complex salt type monoazo dyes, diazo dyes, phthalocyanine dyes, triaryl methane dyes, and other dyes such as sublimable dyes, organic pigments, and the like.

Examples of those hydrophobic dyes applicable to the present invention are given by colors below:

Yellow dyes:

C.I. Solvent Yellow 19 (C.I. 13900A), C.I. Solvent Yellow 21 (C.I. 18690), C.I. Solvent Yellow 61, C.I. Solvent Yellow 80, and Aizen Spilon Yellow GRH Special (manufactured by Hodogaya Chemical Co., Ltd.), Diaresin Yellow F (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Yellow A (manufactured by Mitsubishi Chemical Industries, Ltd.), and Yellow fluer G (manufactured by Sumitomo Chemical Co., Ltd.).

Orange dyes:

C.I. Solvent Orange 1 (C.I. 11920), C.I. Solvent Orange 37, C.I. Solvent Orange 40, Diaresin Orange K (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Orange G (manufactured by Mitsubishi Chemical Industries Ltd.), and Sumiplast Orange 3G (manufactured by Sumitomo Chemical Co., Ltd.).

Red dyes:

C.I. Solvent Red 8 (C.I. 12715), C.I. Solvent Red 81, C.I. Solvent Red 82, C.I. Solvent red 84, C.I. Solvent Red 100, Orient Oil Scarlet #308 (manufactured by Orient Chemical Industries Co., Ltd.), Soldan Red 3R (manufactured by Chugai Chemical Co., Ltd.), Diaresin Red S (manufactured by Mitsubishi Chemical Industries, Ltd.), Sumiplast Red AS (manufactured by Sumitomo Chemical Co., Ltd.), Diaresin Red K (manufactured by Mitsubishi Chemical Industries, Ltd.), Sumiplast Red 3B (manufactured by Sumitomo Chemical Co., Ltd.), Diaresin Red EL (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Red H (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Red LM (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Red G (manufactured by Mitsubishi Chemical Industries, Ltd.), and Aizin Spilon Red GEH Special (manufactured by Hodogaya Chemical Co., Ltd.).

Pink dyes:

Diaresin Pink M (manufactured by Mitsubishi Chemical Industries, Ltd.), and Sumiplast Pink R. FF (manufactured by Sumitomo Chemical Co., Ltd.).

Violet Dyes:

C.I. Solvent Violet 8 (C.I. 42535B), C.I. Solvent Violet 21, Diaresin Violet A (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Violet D (manufactured by Mitsubishi Chemical Industries, Ltd.), and Sumiplast Violet RR (manufactured by Sumitomo Chemical Co., Ltd.).

Blue dyes:

C.I. Solvent Blue 2 (C.I. 42563B), C.I. Solvent 11 (C.I. 61525), C.I. Solvent blue 25 (C.I. 74350), C.I. Solvent Blue 36, C.I. Solvent blue 55, Aizen Spilon Blue GNH (Hodogaya Chemical Co., Ltd.), Diaresin Blue G (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Blue C (manufactured by Mitsubishi Chemical Industries, Ltd.), Diaresin Blue J.A.H.K.N. (manufactured by Mitsubishi Chemical Industries, Ltd.), and Vali Fast Blue #2604 (manufactured by Orient Chemical Industries Co., Ltd.).

Green dye:

C.I. Solvent Green 3 (C.I. 61565).

Brown dyes:

C.I. Solvent Brown 3 (C.I. 11360) and Diaresin Brown A (manufatured by Mitsubishi Chemical Industries, Ltd.).

Black dyes:

C.I. Solvent Black 3 (C.I. 26150), C.I. Solvent Black 5 (C.I. 50415), C.I. Solvent Black 7 (C.I. 50415), C.I. Solvent Black 22, C.I. Acid Black 123 (C.I. 12195), Sumisol Black AR sol (manufactured by Sumitomo Chemical Co., Ltd.), and Vali Fast Black #1802 (Orient Chemical Industries Co., Ltd.).

The above-enumerated hydrophobic dyes are only typical examples, and besides these, for example, those hydrophobic dyes for use in photographic materials for the silver dye bleach process and for the diffusion transfer process may also be effectively used in the present invention.

Further, hydrophobic dyes to be used in the present invention may be those obtained by such a procedure that the dye, in the form of a dye precursor, is dispersed in a polyurethane latex, and after that the dye precursor is made to be a dye by such physical and chemical means as heat treatment, pH control or the addition of a color developing agent, etc. An example of the precursor exemplifies a photographic coupler, while that of the colour developing agent exemplifies a photographic color developing agent.

Those polyurethane latexes impregnating dyes to be used in the present invention may be produced by various methods. As an example, there may be cited those procedures for the impregnation of a hydrophobic material into a vinyl polymer latex as described in U.S. Patent No. 4,199,363, British Patent Publication Open to Public Inspection (hereinater referred to as British Patent O.P.I. Publication) No. 2,003,486, Japanese Patent O.P.I. Publication Nos. 137131/1978 and 50240/1980. In accordance with such methods, in place of the vinyl polymer latex, a polyurethane latex of the present invention is to be used; that is, a dye (hereinafter representing hydrophobic dyes) is first dissolved into an appropriate water-miscible organic solvent to thereby prepare a hydrophobic dye solution, which is then mixed with a polyurethane latex, and after that, from the mixture the water-miscible organic solvent is removed, thereby impregnating the hydrophobic dye in the latex particle.

A particularly preferred method is such that a water-miscible organic solvent is first mixed with a polyurethane latex, and to the prepared solution is added a hydrophobic dye in the solid or liquid state as it is, and stirring is continued. After the solid or liquid phase of the hydrophobic dye alone disappears, the water-miscible organic solvent is removed, thus impregnating the hydrophobic dye into the latex particles.

Useful water-miscible organic solvent is exemplified acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, dimethyl formamide, methyl-ethyl ketone, tetrahydrofuran, N-methyl-pyrolidone, dimethyl sulfoxide, and the like.

A preferred method for impregnating a hydrophobic dye into latex particles has been described as in above, but in addition to this, alternative methods may certainly be used. For example, a hydrophobic dye and a polyurethane latex are selected so that the hydrophobic dye is soluble in the monomer or prepolymer that will be for use in the production of the polyurethane latex. If the dissolved hydrophobic dye is used to extend the chain of the prepolymer, it is possible to obtain a polyurethane latex containing the hydrophobic dye that is usable in the present invention.

The polyurethane latex containing the hydrophobic dye to be used in the present invention may be allowed to contain, if necessary, for example, such dye stabilizing agents as a ultraviolet absorbing agent, antioxidation agent, and the like, and other additives together with the hydrophobic dye. The ratio by weight of the polyurethane latex to the hydrophobic dye in said latex containing said hydrophobic dye of the present invention is preferably from 0.5:1 to 20:1, and particularly preferably from 0.5:1 to 5:1.

The concentration of polyurethane latex particles in the ink composition of the present invention that contain the hydrophobic dye is desirable, when the whole ink composition is regarded as of 100 parts by weight, to be from 0.5 to 10 parts by weight in consideration of the stability as well as the printing quality.

The ink composition of the present invention may be obtained by the addition of such additives for the ink composition as a wetting agent, a fungicide, a surfactant, a chelating agent, a pH control agent, and the like, to the hydrophobic dye-containing polyurethane latex that has been obtained in the above-described manner. Alternatively, these additives may be allowed to be added to the polyurethane latex liquid prior to the impregnation of the hydrophobic dye. Particularly, the addition of the wetting agent to the latex prior to the impregnation of the hydrophobic dye is advantageous for the purpose of obtaining the ink of a high concentration of said dye.

The wetting agent serves to reduce the vapor pressure of the whole ink and to decrease the evaporation rate of water contained in the ink, and addition of said wetting agent prevents an orifice of a nozzle from being clogged with said ink. Therefore, from the standpoint that the wetting agent is desired to be well-soluble in water, well-water-absorbable and to be capable of highly dispersing the polyurethane latex particle, aliphatic polyhydric alcohols, alkyl ether derivatives of aliphatic polyhydric alcohols, and acetate derivatives of aliphatic polyhydric alcohols are excellent for this purpose. Typical examples is a polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, polyethylene glycol, glycerol, and the like; alkyl ether derivatives of polyhydric alcohols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethel ether, diethylene glycol monobutyl ether, diethylene glycol methyl-ethyl ether, triethylene glycol monomethyl ether, and the like; and acetate derivatives of polyhydric alcohols such as ethylene

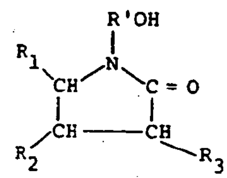
glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, glyceryl monoacetate, glyceryl diacetate, and the like. Further, mixtures of the above-enumerated polyhydric alcohols, alkyl ether derivatives of polyhydric alcohols, and acetate derivatives of polyhydric alcohols.

Among these wetting agents, those whose HLB values are not more than 9.5 are well permeable into ordinary paper, so that when used as permeating solvents they enable to obtain a quick drying ink that is excellent in drying on paper. In this case, however, a wetting agent whose HLB value exceeds 9.5 is desirable to be used together.

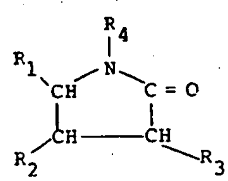
Those preferred as permeating solvents are such dialkyl ether derivatives of polyhydric alcohols as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, and the like.

In the present invention, from 5 to 50 parts by weight of the wetting agent and from 5 to 70 parts by weight of the permeating solvent are desirable to be added, and if they are within the ranges, the viscosity may be arbitrarily adjusted.

In the present invention, there may also be added formamide, N-hydroxyalkyl-2-pyrolidones having the formula:



wherein R' is an alkylene group, R_1, R_2 and R_3 each is an alkyl group, and N-alkyl-2-pyrolidones having the formula:



wherein R_1, R_2, R_3 and R_4 each is an alkyl group.

The addition of these compositions in the quantity of from 1 to 30 parts by weight, respectively, has been known to improve the effect of preventing the clogging phenomenon of the orifice of the nozzle.

As the fungicide for the purpose of preventing the growth of fungi as well as of the storage of the ink over extensive periods, such known fungicides, as dioxine, sodium dehydroacetate, and the like may be used. And for the improvement of the ink in the spread thereof or for the improvement of the latex particles in the dispersion stability thereof, a surfactant may be used. Preferred surfactant is affected by each individual latex and hydrophobic dye used and may, according to circumstances, be anionic, cationic, nonionic or mixed anionic-nonionic. Preferred surfactant exemplifies polyethylene glycol ether having a long chain alkyl; quaternary ammonium salts, tertiary amine salts or alkylolamine salts having long chain alkyl and sulfate; alkyl sulfonic acids, alkylaryl sulfonic acids, and salts of these acids, metallic salts of macromolecular organic acids, and the like. Nonionic surfactants such as, e.g., copolymer of polyoxyethylene and poly(propylene glycol), and nonyl phenoxypolyethyleneoxyethanol are particularly preferred. The adding amount of these surfactants is generally not more than 1% by weight of the whole quantity of the ink composition, and more preferably within the range of from 0.05 to 0.1% by weight.

Various kinds of inorganic or organic buffers may be added to prevent the change in the pH resulting chiefly from the absorption of carbon dioxide in air during the storage of the ink in the container or during the stay of the ink in the nozzle. Those desirable buffer include, carbonates, such as sodium carbonate and potassium carbonate whose appropriate adding amount may be practically from 0.1 to 5% by weight to the whole quantity of the ink composition, and preferably from 0.1 to 2% by weight.

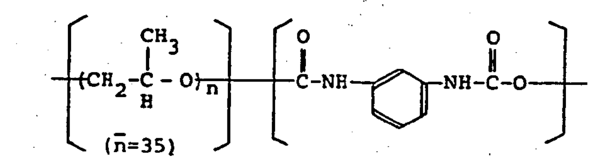
For the purpose of the masking of the metal and metallic ions in the ink composition, various chelating agents may be added, typical examples of which include sodium gluconate, ethylenediaminetetraacetic acid (EDTA), disodium salt of EDTA, trisodium salt of EDTA, tetrasodium salt of EDTA, sodium salt of diethylene-triaminopentaacetic acid, and the like.

The present invention is illustrated with reference to examples below, which are to illustrate in further detail, but the embodiment of the present invention is not limited thereto.

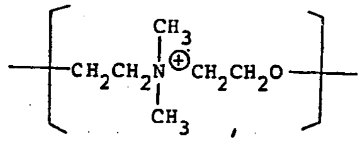
In addition, all the polyurethane latexes used in examples below are those produced in accordance with the procedures as described in U.S. Patent No. 3,873,484.

EXAMPLE 1

To 100 g of a polyurethane latex (solid matter concentration: 6% by weight) having a following composition was added 100 g of acetone and 10 g of ethyl acetate, and to the mixture, with stirring, was slowly added 6 g of C.I. Solvent Blue 2 (C.I. No. 42563B). The obtained mixture was dissolved uniformly and after that, the solvent was removed by means of an evaporator, whereby a hydrophobic dye-containing aqueous dispersed liquid having the dye concentration of 6% by weight was obtained.



16.7 66.6



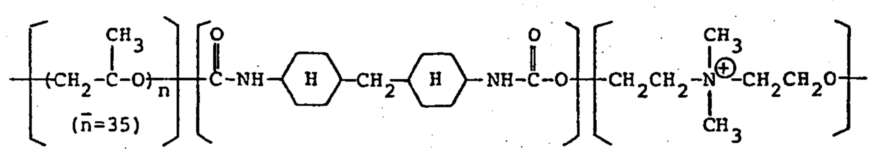
16.7 mol% (the same applies hereinafter)

To the aqueous dispersed liquid was added 92 g of tetraethylene glycol diethyl ether, 36 g of triethylene glycol, and 12 g of 10% by weight potassium carbonate, and the mixture was uniformly mixed. The thus obtained ink composition of the present invention was able to be filtrated without clogging through Toyo Filter Papter No. 131 (manufactured by Toyo Filter Paper Co., Ltd.).

The ink composition of the present invention has the viscosity of 7.3 centipoise (cps) at room temperature (25°C) and surface tension of 42.5 dyn/cm, and had no change in the characteristics even after the one-month storage thereof, during which no deposits was recognized.

EXAMPLE 2

6 g of C.I. Solvent Red 8 (C.I. No. 12715) was dissolved into 150 g of acetone and to the obtained solution, with stirring, was slowly added dropwise 100 g of a polyurethane latex (solid matter concentration: 8% by weight) having the following composition. After the whole quantity was added dropwise, the solvent was removed by means of an evaporater, thereby obtaining a hydrophobic dye-containing polyurethane latex having the dye concentration of 6% by weight.



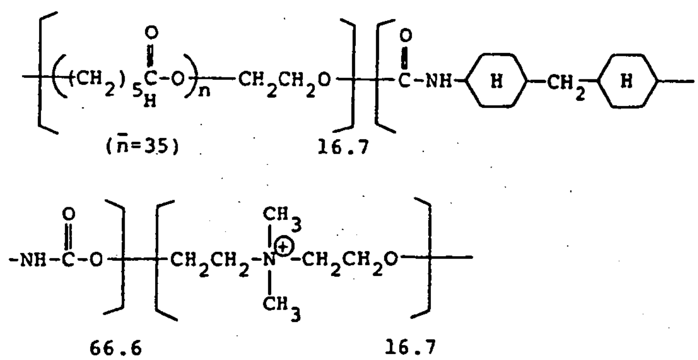
16.7 66.6 16.7

To the obtained aqueous dispersed liquid was added 92 g of diethylene glycol monobutyl ether, 36 g of polyethylene glycol #400, and 12 g of 10% by weight potassium carbonate, and the mixture was uniformly mixed. The thus obtained ink composition of the present invention was able to be filtered without clogging through a Toyo Filter Paper No. 131. This ink composition of the present invention has the viscosity of 7.6 cps. at room temperature (25°C) and surface tension of 30.5 dyn/cm, and had no change in the characteristics even after the one-month storage thereof, during which no depostis was recognized.

EXAMPLE 3

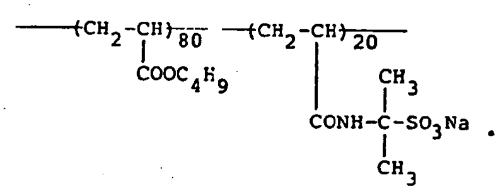
To 100 g of a polyurethane latex (solid matter concentration: 10% by weight) having the following composition was added 100 g of tetraethylene glycol dimethyl ether, 37.5 g of glycerol, and 250 g of tetrahydrofuran, and to the mixture, with stirring, was slowly added 10 g of a blue hydrophobic dye [2-tert-butylsulfamoyl-4-(2-methyl-sulfonyl-4-nitrophenylazo)-5-(3-aminosulfonyl-benzene-sulfoneamide)-1-naphthol], and the resulting mixture was dissolved uniformly. After that, the tetrahydrofuran was removed by means of an evaporator, and finally 12.5 ml of 10% by weight

potassium carbonate was added to thereby obtain a hydrophobic dye-impregnated polyurethane latex with the dye concentration of 4% by weight wherein the ratio by weight of the hydrophobic dye to the polyurethane latex equals 1:1. The ink composition of the present invention finally obtained by being filtrated through a Toyo Filter Paper No. 131 has the viscosity of 8.0 cps. at room temperature (25°C) and surface tension of 38.3 dyn/cm, and even after the one-month storage of the ink no deposits were observed.



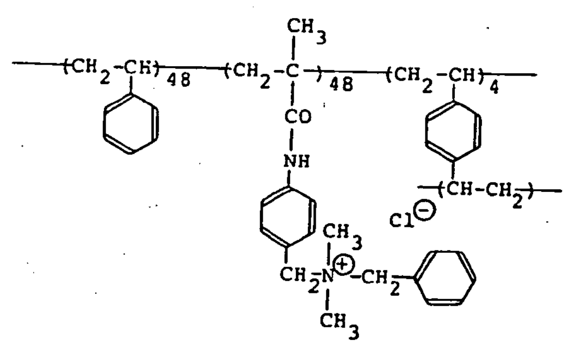
CONTROL 1

The procedure of Example 1 was repeated the same with the exception that in place of the polyurethane latex, a polyvinyl polymer latex having the following composition was used, but the obtained ink was shown a large amount of deposits after the one-week storage thereof.



CONTROL 2

For another comparison, a vinyl polymer latex having the following composition was used to carry out the same procedure as in Example 3, then the dye was not completely impregnated, thus partially deposited. In addition, the ratio of the impregnated amount of the hydrophobic dye to the polymer latex was found to be 0.67:1.



EXAMPLE 4

The foregoing ink composition that have been obtained in the examples and the control examples were used to carry out ink printing by the use of an ink-jet printing apparatus specified in Figures 1 to 3 disclosed U.S. Patent No. 4,189,734, the apparatus being adjusted to the parameter given in Table 1. The results that were obtained by the printing were as shown in Table 2. As apparent from the table, the ink composition of the present invention was excellent.

TABLE 1

Printing speed	2,000 dots/sec.
Static pressure	-4.9×10^{-3} Kg/cm^2
Peak pressure of pulse	1.8 Kg/cm^2
Pulse voltage	120 V
Pulse width	110 μs
Diameter of orifice	0.076 mm.

TABLE 2

Ink composition	Drying speed[1)] on paper*	Dot quality			Clogging after 10-hour storage in the room
		Density[2)]	True roundness	Gloss	
Ink of Example 1	Within 3 seconds	1.61	good	glossy	None
Ink of Example 2	Within 3 seconds	1.49	good	glossy	None
Ink of Example 3	Within 3 seconds	1.82	good	glossy	None
Ink of Control 1	Within 3 seconds	1.59	good	glossy	Clogged
Ink of Control 2	Within 3 seconds	1.30	good	glossy	None

Note: * A recording paper whose sizing degree is 23 seconds in accordance with the stoechigt testing method (JIS P—8122).

1) Such period that the ink, after recording, becomes not rubbed off any hand.
2) Spectral reflection density of each dye in the overall-printing area.

CLAIMS

1. An ink composition for ink-jet printing which comprises an aqueous medium in which are dispersed particles of a polyurethane latex containing a dye.

2. An ink composition according to Claim 1, wherein the dye is a hydrophobic dye.

3. An ink composition according to Claim 1 or Claim 2, wherein the polyurethane latex comprises a polyurethane that is derived from a polyol and an isocyanate.

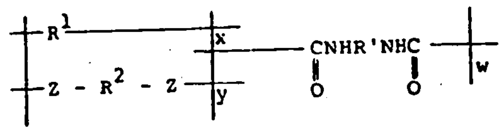
4. An ink composition according to Claim 3, wherein the polyol is a prepolymer or a prepolymer mixture having repeating units derived from an alkyl ether or ester having at least two hydroxy groups and a molecular weight of from 300 to 20,000.

5. An ink composition according to Claim 3 or 4, wherein the isocyanate has the formula:

$$O=C=N-R-N=C=O$$

in which R represents an alkylene, cycloalkylene, arylene, alkylene-bisarylene, or arylene-bisalkylene group.

6. An ink composition according to Claim 1 or 2 wherein said polyurethane latex is represented by a formula:



wherein R represents an alkylene group which may have a hetero atom or hetero atoms, an cycloalkylene group, an arylene group, an alkylene-bisarylene group, or an arylene-bisalkylene group; R^1 represents

$$-(ZR^3)_m-(Z-(\underset{\underset{O}{\|}}{C})_m R^4)_n-Z- \quad \text{or}$$

$$-Z-(R^5-Z-\underset{\underset{O}{\|}}{C}-R^6-\underset{\underset{O}{\|}}{C}-Z)_p R^5-Z-;$$

R^2, R^3 and R^5 each represent an alkylene group which may have a substituent or substituents; R^4 represents an alkylene group having from 2 to 10 carbon atoms; R^6 represents an alkylene group having from 2 to 10 carbon atoms or an arylene group; each Z represents —O— or —NH—; p and n each represent an integer from 2 to 500; m represents 0 or 1; y represents from 0 to 90 mole % of the diol; x represents from 100 to 10 mole % to the y; and w represents from 1.1 to 2.0.

7. An ink composition according to any of the preceding Claims wherein the weight ratio of polyurethane latex to dye is from 0.5:1 to 20:1.

8. An ink composition according to any of the preceding Claims which comprises from 0.5 to 10 wt.% of the polyurethane latex.

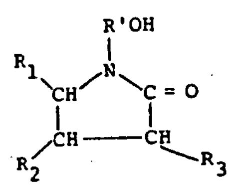
9. An ink composition according to any of the preceding Claims which comprises a wetting agent, fungicide, surfactant, chelating agent, and/or pH control agent.

10. An ink composition according to Claim 9 which comprises 5 to 50 parts by weight of the wetting agent.

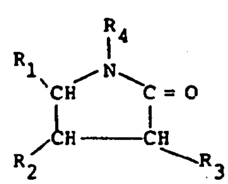
11. An ink composition according to Claim 9 wherein the wetting agent has an 1+LB value exceeding 9.5.

12. An ink composition according to Claim 11 which comprises 5 to 70 parts by weight of the wetting agent.

13. An ink composition as claimed in any of the preceding Claims which comprises 1 to 30 parts by weight of formaldehyde, an N-hydroxyalkyl-2-pyrrolidone of the formula (A) or an N-alkyl-2-pyrrolidone of the formula (B).



(A)



(B)

in which formulae
R′ is an alkylene group, and
R_1, R_2, R_3 and R_4, which may be the same or different, are each an alkyl group.

14. An ink composition according to Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 4.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.